

Metastability of Molecular Phases of Nitrogen: Implications to the Phase Diagram

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Anomalous Molecular Phase of Nitrogen: Implications to the Phase Diagram

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Despite their simplicity, diatomic molecules of first row elements can exhibit very complex phase diagrams. Determination of the phase diagrams can be further complicated by the existence of hysteretic molecular phases that can be observed over large regions of coexistence. Here we present evidence for a previously unreported molecular phase of nitrogen existing at room temperature at least over the range of 33 – 74 GPa. Our measurements show that sample history may have a significant impact on the thermodynamic states accessed by the molecular nitrogen solid and, by extension, also on the established phase diagram.

Keywords: High Pressure; Nitrogen; Molecular solid; Phase transformation; Raman Spectroscopy

1. Introduction

Study of the high-pressure phases of molecular nitrogen has been a longtime focus of high-pressure research. Over the last few decades, the phase diagram of the molecular solid has been measured over a wide range of temperatures and pressures [1-8]. While the phase diagram appears to be well established for pressures lower than ~20 GPa, the nature of the molecular phases for higher pressures remains controversial. Specifically, powder x-ray diffraction as well as optical characterizations have been used for structural determinations in nitrogen. However, recent spectroscopic investigations employing Raman and infrared techniques have demonstrated intricacies in the higher pressure modifications that had not been previously reported. For example, published room-temperature x-ray data are consistent with the $R\bar{3}c$ structure or the ϵ -phase for pressures between 16 and at least 49 GPa [9]. On the other hand, the Raman data appears to be incompatible with this latter structure for pressures above 25 GPa [3, 10, 11]. Similarly, recent literature questions a previously reported transition at ~20 GPa from the $\epsilon \rightarrow \eta$ phase [1, 12]. In this case, the structural modifications are probably subtle distortions or close derivatives of the ϵ phase, based on x-ray signatures and the similarity of optical spectra. Clearly, the possible presence of near-degenerate structures would complicate the understanding of the equilibrium phase diagram. Such structures would lead, for instance, to hysteresis and history-dependent phases. Evidence for this can be found both in theory and experiment. In calculations for pressures between 20 and 30 GPa both the cubic and tetragonal structures are found to coexist [13]. A similar kind of hysteresis at low temperature ($T < 90$ K) has been observed experimentally by Bini *et al.* in the ϵ -phase [1]. Additionally, Buchsbaum *et al.* noted a hysteretic regime of about 20 K between the β - and the δ -phases [2]. Thus, the phenomenon of low temperature hysteresis in simple molecular solids is not unusual. However, occurrence of multiple crystallographic structures for a given pressure regime at room temperature in first-row molecular solids is uncommon. We report here the occurrence of a previously undocumented phase that was observed at *room temperature* at 74 GPa and persisted during pressure release to a pressure lower than 33 GPa. The observation of this phase supports the existence of near-degenerate phases in molecular nitrogen and suggests that determining the equilibrium phase diagram may require further understanding about the existence and nature of these hysteretic phases.

2. Experimental Technique

The Raman spectra shown in Fig. 1 were recorded at room temperature in a backscattering geometry using the 488 nm line from an argon ion laser. The instrumental resolution in these experiments was $\sim 3.5 \text{ cm}^{-1}$. The particular anomalous samples described here were prepared by standard DAC techniques described elsewhere [14]. The gasket was precompressed and a small hole of $\sim 60 \text{ }\mu\text{m}$ was drilled in the center. The anomalous nitrogen samples were loaded cryogenically, and the pressure was determined using the fluorescence from multiple ruby chips within the samples. The Raman signatures reported here were collected at several steps in decreasing pressure to 9.6 GPa and subsequently on pressure increase to 30 GPa. Several other runs were performed that were initially loaded at pressures between 2 and 14 GPa. These latter samples yielded only previously reported “normal” spectra and were measured only in increasing steps of pressure.

3. Results

Figure 1 shows the anomalous and the equivalent normal Raman vibron spectra for molecular nitrogen at pressures of $\sim 74 \text{ GPa}$ and $\sim 33 \text{ GPa}$, respectively. Both sets of vibron spectra exhibit striking differences in relative integrated intensities, peak amplitudes, and band frequencies. It is clear that the anomalous spectra differ markedly from any previously reported in the literature. Upon decompression, the sample appeared to convert to the δ -phase by 9.6 GPa as indicated by two vibronic excitations at 2354 and 2365 cm^{-1} [3,4]. We thus bracketed this transformation as occurring above 9.6 and below 32 GPa. Upon subsequent compression to 30 GPa, the sample exhibited normal spectra consistent with previous studies.

The vibron structure of the anomalous sample at 74 GPa differs markedly from a normal sample not only in intensities but also in spectral band frequencies. With good signal-to-noise one can observe five to six peaks for a normal sample under these conditions [15]. In the anomalous sample, the two lower energy bands in Fig. 1 are observed $\sim 30 \text{ cm}^{-1}$ lower than any band reported at this pressure. One may note that a weak similarity exists in the signatures from the anomalous phase and the ϵ -like structure observed in a normal sample at lower pressures. The slightly narrower linewidths for the vibrons in the anomalous *vis-a-vis* the normal phase suggest that the sample did not experience unusual pressure broadening or gradients even at 74 GPa.

4. Discussion

We now discuss the nature of the anomalous phase, which we suggest is a new, hysteretic modification of molecular nitrogen. Support for this conclusion can be garnered from two observations. Firstly, the vibron band frequencies are markedly different in frequencies from normal suggesting that the observations cannot be explained simply as a linear combination of mixed phase signatures, but rather involve different factor-group interactions. Secondly, the fact that we could induce the anomalous sample to convert and yield normal Raman signatures by decreasing pressure and subsequently recompressing support the notion that the sample may have been kinetically frozen in an alternate phase. More work clearly needs to be performed in order to ascertain the thermodynamics and kinetics of the high pressure phases.

Without more information than currently available, we cannot provide definitive identification of the crystallographic structure of the anomalous phase. We speculate here as to possible space groups that would be consistent with our data, namely three main vibron modes. Through fitting procedures, one can obtain somewhat better fits to the data if one assumes the existence of more bands. However, we do not have confidence that the assumption of more bands is physically justifiable at this time. At 80 K, the accepted phase diagram indicates that a normal sample would traverse through β -, γ -, δ_{loc} -, ϵ - and the ζ -phase stability regions with increasing pressure. Accordingly, one can argue that these structures might

be possible candidate structures for the anomalous phase. The crystal structures of the β - and γ -phases ($P6_3/mmc$ and $P4_2/mnm$, respectively) can be ruled out since the β and γ phases support only one and two stretching modes, respectively [5]. Even though the cubic α -phase ($Pa3$ structure with 4 molecules per unit cell) is not encountered at 80 K, the structure can also be ruled out based on the two supported stretching modes [5].

On the other hand, several of the other crystallographic structures found in molecular nitrogen are consistent with our data. The crystallographic structures of the δ , ϵ , and ζ phases permit three, three, and five stretching modes, respectively. Finally, there are also several tetragonal structures for high pressure phases of molecular nitrogen either assumed or theoretically predicted [6, 13]. These also offer more modes than necessary to account for our observations, namely permitting up to 5 distinct Raman-active vibrons. We note that the $Pm3n$ (δ -phase) arrangement has the highest symmetry of the nitrogen structures consistent with the anomalous spectra reported in this work.

5. Conclusions

In summary, our measurements indicate that there is at least one previously unreported structure of the nitrogen molecular solid that can exist over a wide pressure range between 33 and at least 74 GPa at room temperature. The Raman signatures are consistent with several known structures of molecular nitrogen, of which the $Pm3n$ is the highest symmetry candidate. It is possible that even more molecular phases can be prepared that are dependent on preparation history. We thus conclude that sample history may play an important role in the interpretation of data and conclusions drawn about the phase diagram in molecular nitrogen.

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List of Figures

FIGURE 1 Raman spectra of vibrons measured in anomalous and normal samples at pressures of ~74 GPa (top) and ~33 GPa (bottom), respectively.

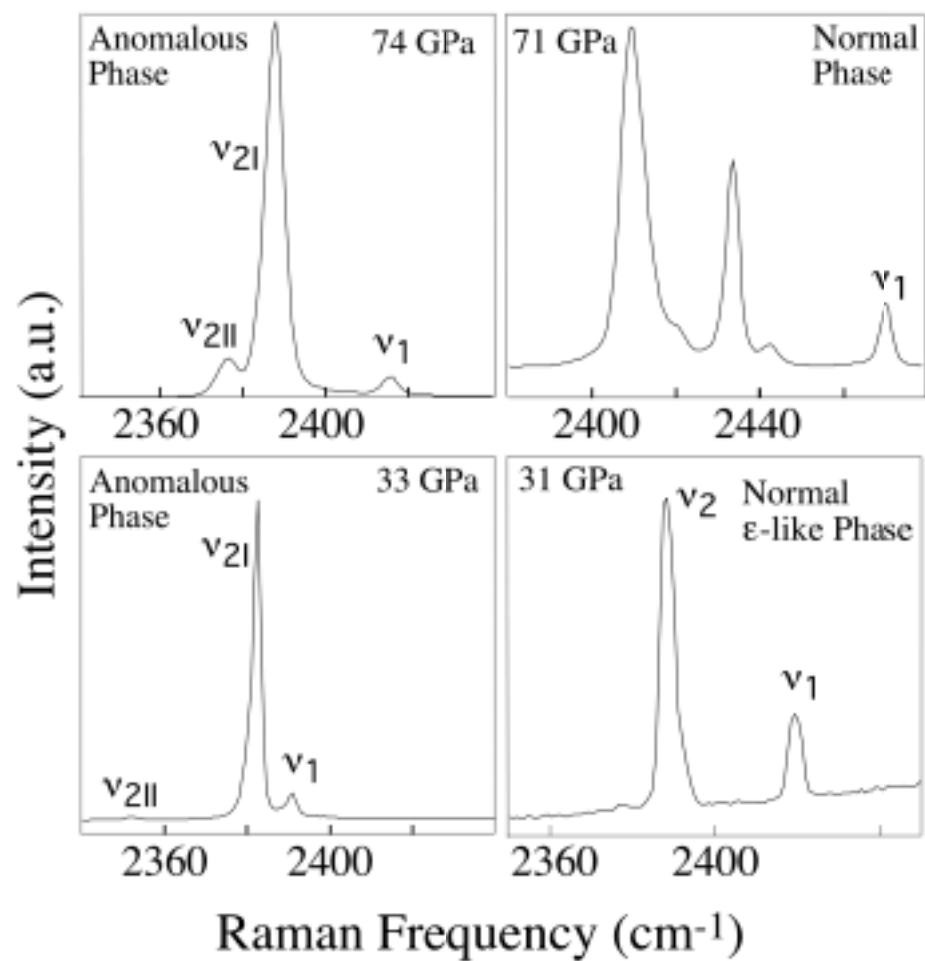


FIGURE 1 Lorenzana et al.

[illegible]